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Fine particulate ($PM_{2.5}$) composition in Atlanta, USA: assessment of the particle concentrator-Brigham Young University organic sampling system, PC-BOSS, during the EPA supersite study

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Abstract

Aerosol concentrations of carbonaceous material, sulfate, and nitrate for samples obtained using a newly designed PC-BOSS are reported. The results indicated that $PM_{2.5}$ composition in Atlanta was dominated by sulfate and organic material, with low concentrations of particulate nitrate. Observed average particulate component concentrations for the 26-day study period were: sulfate, $12.2 \mu\text{g}/\text{m}^3$ ($17.0 \mu\text{g}/\text{m}^3$ as ammonium sulfate); non-volatile organic material, $11.4 \mu\text{g OM}/\text{m}^3$ (assumes organic material, OM, is 61% C); semi-volatile organic compounds (SVOC) lost from particles during sampling, $5.3 \mu\text{g OM}/\text{m}^3$; filter retained nitrate, $0.1 \mu\text{g}/\text{m}^3$ ($0.2 \mu\text{g}/\text{m}^3$ as ammonium nitrate); nitrate lost from particles, $0.3 \mu\text{g}/\text{m}^3$ ($0.4 \mu\text{g}/\text{m}^3$ as ammonium nitrate); and soot (elemental carbon), $1.5 \mu\text{g}/\text{m}^3$. The PC-BOSS particle concentrator efficiency was obtained by comparison of the PC-BOSS sulfate data with sulfate data obtained from the Federal Reference Method (FRM) sampler. A modification of the PC-BOSS design to allow independent determination of this parameter is recommended. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Correct assessment of the factors associated with the effects of $PM_{2.5}$ on human health, visibility impairment and climate-related radiation balance is dependent on the accurate determination of the chemical composition of particles present in the atmosphere. Major inorganic components of the fine fraction of atmospheric aerosols are sulfate, nitrate and ammonium ions. In most urban areas the fraction of these components ranges up to 60% of the total suspended particulate matter (Hightower and Richardson, 1988). Because of the concern over the visibility reduction and adverse health effects associated with sulfates and nitrates in atmospheric aerosols, the concentration of these species have been monitored in a

number of field programs in order to study their diurnal fluctuations and to determine the relative importance of the contributions from various emission sources. Examination of data from numerous studies (Hidy, 1974) has shown that in a number of instances there is an inverse relationship between the concentrations of sulfate and nitrate in particulate samples. These ambient observations continued to motivate further studies to confirm that the variations were due to a real chemical effect rather than some other cause such as advection of air masses from different sources, and to obtain information on the chemical mechanism(s) which decreases the observed nitrate concentrations when processes involving the formation of sulfate compounds are important. Subsequent studies did however show that early nitrate data included uncertainties reflecting two types of errors. A positive bias resulting from adsorption of nitric acid on alkaline filters and from

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reaction of nitric acid with particulate salts during sampling (Spicer and Schumacher, 1977). Negative bias resulted from displacement of ammonium nitrate from particles by acids e.g., HCl (Appel and Tokiwa, 1981) and H₂SO₄ (Harker et al., 1977), and from thermal instability of nitrate salts such as ammonium nitrate (Stelson et al., 1979) which can decompose to give gaseous ammonia and nitric acid. At ambient humidities lower than the deliquescent point of NH₄NO₃, significant amounts of particulate ammonium nitrate can be lost by volatilization from particles collected on filters (Forrest et al., 1980; Appel et al., 1980b; Eatough et al., 1999; Cass and Hering, 1999). These negative artifacts can lead to measured atmospheric nitrate concentrations which are less than half of the true atmospheric particulate nitrate.

Besides problems of underestimation or overestimation resulting from the processes described above, numerous studies are also available which document the retention of atmospheric SO₂ and nitrogen oxides on filter media. Such retention also leads to measurements of atmospheric sulfate and nitrate concentrations that are too high (Lee and Wagman, 1966; Spicer, 1977; Spicer and Schumacher, 1977; Witz and Wendt, 1981). These artifacts are minimal for an inert filter, e.g. Teflon.

Urban aerosols also contain a significant fraction of carbonaceous material directly emitted from stationary and automotive sources (primary particulate carbon, both elemental and organic) or formed in the atmosphere by photo-oxidation of gaseous hydrocarbons (secondary particulate organic carbon). Concern about organic carbon, both primary and secondary, originates from human health considerations, since organic extracts of urban aerosols have been shown to be mutagenic and carcinogenic in a number of bioassays and animal studies (Kelly et al., 1994). Important among these mutagens and carcinogens are semi-volatile organic compounds formed from wood smoke and motor vehicle emission chemistry (Pederson and Siak, 1981; Lewis et al., 1991).

Semi-volatile organic compounds (SVOC) are compounds expected to be present in the atmosphere in both the gaseous and particulate phases (Pankow, 1987; Ligocki and Pankow, 1989). Gas phase SVOC and fine particulate SVOC are expected to have different environmental effects. For example, toxic SVOC on fine particles will be deposited differently than gases in the respiratory tract and may be associated with particulate health effects (Pope et al., 1995; Schwartz et al., 1996), and fine particulate SVOC are expected to scatter light and therefore contribute to visibility reduction (Eatough et al., 1996; Pratsinis et al., 1984). Again, filter sampling procedures for particles suffer negative sampling artifacts due to loss of particulate SVOC (Eatough, 1999) and positive sampling artifacts from the adsorption of gas phase organic material by the sampling filter or

collected particles (Eatough, 1999; McDow and Huntzicker, 1990). Even though filter/adsorbent samplers may be used for the measurement of the total concentration of organic compounds in the atmosphere, these samplers will not determine the correct phase distribution of SVOC.

In spite of the widespread recognition of these artifact phenomena, atmospheric sampling continues with samplers and techniques for which significant errors in ambient particulate nitrate and organic material concentrations are to be expected. In view of such potential anomalies, this article describes the use of the PC-BOSS sampler for the determination of ambient concentrations of particulate nitrate and organic material including fine particulate SVOC with minimum artifact contribution. This study is part of the summer US EPA Supersite study in Atlanta, Georgia, USA, from 3 August 1999 through 30 August 1999 (Solomon et al., 2000).

2. Experimental

2.1. Sampling protocol

Two PC-BOSS samplers were used at the August 1999 Atlanta EPA Supersite program. Samples to evaluate the determination of fine particulate composition and concentrations were collected on various time schedules. Two 12 h samples were collected during even numbered days from 7:00 a.m. to 7:00 p.m. and from 7:00 p.m. to 7:00 a.m. EDT the next day, and 24 h samples were collected during odd numbered days from 7:00 a.m. to 7:00 a.m. EDT the next day using a PC-BOSS. Collocated samples were collected using a second PC-BOSS that was similarly configured as described below. This second PC-BOSS was also used for collecting blank samples as well as for measurement of the denuder efficiency for collection of gas phase organic species.

2.2. The PC-BOSS sampling system

Fig. 1 shows the schematic of the PC-BOSS used in Atlanta. The inlet to the sampler is a Bendix cyclone (Chan and Lippmann, 1977) with a particle cut of 2.3 µm aerodynamic diameter at an inlet flow of 150 l/min. Following the inlet, 16 l/min of the total flow was diverted to the side flow manifold holding a single filter pack containing a Teflon and a charcoal-impregnated cellulose filter (CIF). In earlier designs of the PC-BOSS (Eatough et al., 1999) there was no side flow system as shown in Fig. 1. The side flow filter was intended to allow determination of the particle concentrator efficiency and losses.

The remainder of the sampled air stream entered a virtual-impactor particle concentrator. The design and evaluation of the concentrator have been previously

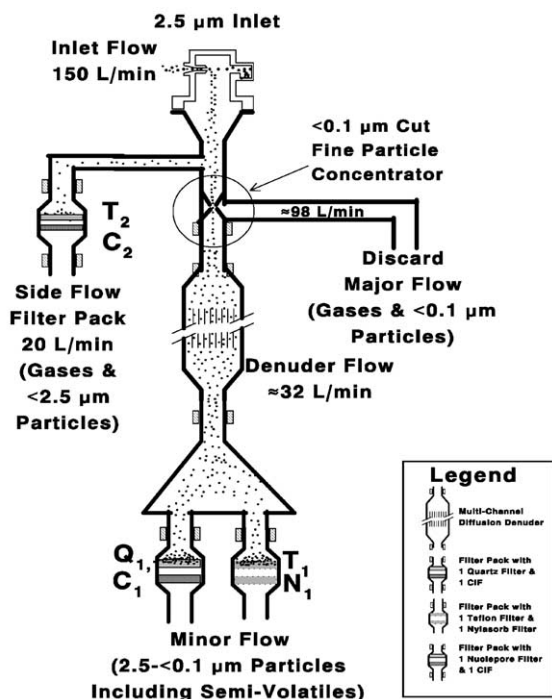


Fig. 1. Schematic of the newly-designed PC-BOSS used in Atlanta.

described (Ding et al., 2001; Sioutas et al., 1994). The particle concentrator separates 75% of the gas phase material into the major flow (earlier designs of the PC-BOSS had a quartz filter at the major flow, however, the present design has no filter in the major flow) and leaves particles larger than the cut point (about $0.1\ \mu\text{m}$) along with a significantly reduced fraction of the gas phase material in the minor flow. Thus, the particle concentrator gives rise to a concentrated stream of $0.1\text{--}2.3\ \mu\text{m}$ particles in the minor flow of the PC-BOSS.

The minor flow air containing concentrated particles enters the BOSS diffusion denuder (Eatough et al., 1993). The denuder is comprised of 15 strips ($4.5 \times 58\text{ cm}^2$) of Schleicher and Schuell charcoal impregnated cellulose filter which are separated at the long edges by 2 cm diameter glass rods. The multi-parallel plate array of filter strips is contained within a rectangular aluminum tube. The entire arrangement is nominally 90 cm in length to accommodate the 58 cm adsorbent filter strips and two nominally 15 cm long flow straightening sections ahead of and behind the denuding section. The denuder strips are cut from the filter sheets as received from the manufacturer without any pre-treatment, and the useful lifetime of the denuder at a flow rate of 40 l/min is about 3 months (Cui and Eatough, 1998; Eatough, 1999). As sampled air passes through the denuder, gas phase species compete with each other for denuder adsorption sites. With about

75% of gas phase species in the sampled air removed in the particle concentrator prior to passage of the aerosol through the denuder, denuder efficiency for SVOC, SO_2 and HNO_3 is expected to exceed 99% (Eatough et al., 1999; Ding et al., 2001; Pang et al., 1999). As a result, positive sampling artifacts from the collection of gas phase organic compounds and nitric acid by quartz filters or sorbent filters after the denuder are expected to be negligible. In spite of these strengths, one drawback of using CIF as the denuder material is that the adsorbed gas phase organic material cannot be determined because of the high carbonaceous material blank of the CIF (Lewtas et al., 2001).

The denuder was followed by two parallel filter packs. One of the parallel filter packs contained a 47-mm quartz filter (Gelman Sciences, Ann Arbor, MI, USA) followed by a 47-mm charcoal impregnated filter (CIF, Schleicher and Schuell, Keene, NH, USA). This combination of filters was used to determine fine particulate carbonaceous material, sulfate, and stable nitrate on the quartz filter, and semi-volatile nitrate and organic material lost from the particles on the quartz and trapped on the sorbent CIF. The other parallel filter pack contained a 47-mm Teflon (Gelman Tefluor or Zefluor, or Whatman Tefluor) followed by a Nylasorb filter (Gelman Nylasorb). The Teflon filter was used to determine mass, sulfate and stable nitrate, whereas the nylasorb filter was used for the determination of nitrate lost from particles during sampling. With this combination of techniques negative sampling artifacts are avoided.

All quartz filters were baked at 800°C for 24 h before use. The CIF sorbent filters used in this study underwent an extensive cleanup by first extracting three times each with methanol and dichloromethane, followed by a complete removal of residual organic solvent using a vacuum oven at 140°C . The Teflon and Nylasorb filters were used as received from the manufacturer. The CIF strips in the BOSS denuder were also used as received from the manufacture.

3. Sample analysis

3.1. Analysis for nitrate and sulfate

Sulfate and nitrate analysis was by ion chromatography. All ion chromatographic analysis was performed using a Dionex LC20 Chromatograph equipped with a CD20 conductivity detector. The eluent was $3.5\text{ mM Na}_2\text{CO}_3/1.0\text{ mM NaHCO}_3$ solution at a flow rate of 1.2 ml/min , and the suppressor was an anion self-regenerating suppressor. One 2-cm^2 punch of the quartz filters was extracted by ultrasonication with 5-ml deionized water in a 10-ml monovette (Sarstedt, Newton, NC, USA). The extracted solution was analyzed for

sulfate and nitrate. Whole Zefluor or Tefluor filters were also extracted by ultrasonication in 10-ml deionized water in a 10-ml monovette and analyzed for sulfate and nitrate. One 2-cm² punch of the CIF filters was extracted by ultrasonication in 5-ml of a 1% acetone-eluent solution (Ding et al., 2001) in a 10-ml monovette and analyzed for nitrate. Whole nylasorb filters were extracted ultrasonically in 10-ml eluent solution in a 10-ml monovette and analyzed for nitrate.

3.2. Analysis of collected carbonaceous material

Two centimeter square portion of the quartz and CIF filters were analyzed for carbonaceous material by thermal desorption of the collected materials using temperature programmed volatilization (Ellis and Novakov, 1982; Tang et al., 1994). The organic compounds and soot were converted to CO₂, which was then determined using a non-dispersive infrared (NDIR) detector on an ULTRAMAT 3-Gas analyzer (Siemens Inc., Roswell, GA, USA). The NDIR detector was calibrated using three certified CO₂ standards which spanned the analysis concentration range. Organic compounds evolved from the particles and collected by the CIF filter will be referred to in this paper as semi-volatile. The carbonaceous material retained by the quartz filter will be referred to as non-volatile. The CIF filters were heated from 50°C to about 300°C at a ramp rate of 10°C/min in a stream of nitrogen. The maximum temperature for the CIF analysis was imposed by the fact that degradation of the filter matrix began 10–20°C below the maximum analysis temperature. The quartz filters were heated from 50°C to 800°C at a ramp rate of 28°C/min in a stream of N₂/O₂ (70:30% v/v). Soot was estimated from the high temperature (usually above 400°C) peak (Ellis and Novakov, 1982) on the thermogram obtained from the quartz filter analysis. Because of the presence of high concentrations of secondary organic material which evolved at a temperature just below that for soot, the precision of this estimate is probably about 30–50%. The shape of the thermograms indicated that all collected organic compounds and soot were evolved from the collection matrix at the maximum temperatures used. No evidence for the high-temperature evolution of CO₂ from inorganic carbonates was seen. Blank determinations were made for both quartz and CIF filters.

4. Results and discussion

4.1. Efficiency of the particle concentrator

The particle concentrator efficiency is an important parameter needed to correct the concentration of species

determined on the minor flow filters of the PC-BOSS to ambient concentration. An appropriate approach to determining this efficiency is by performing a regression analysis using the concentration of stable species such as aerosol sulfate determined in the side flow and minor flow of the system. The side flow sulfate concentration present on the Teflon filter (T_2 in Fig. 1) was compared to sulfate concentrations determined using a PM_{2.5} FRM sampler (Solomon et al., 2000). The PC-BOSS side-flow sulfate concentrations were uniformly biased 15% higher than the PM_{2.5} FRM sulfate data. It was concluded that the distance between the transition from the 3/8 in inlet line to the 1 in tube containing the side flow splitter was insufficient to allow uniform aerosol distribution across the sample tube. Since the side flow was sampled from the center of the flow, this resulted in side-flow concentrations that were biased high. As the side flow was only 10% of the total flow, this bias had only a small effect on the concentrations of material which entered the particle concentrator. For the Atlanta study, the particle concentrator efficiency and losses (Ding et al., 2001) was determined by comparison of PM_{2.5} FRM sulfate and PC-BOSS minor flow sulfate data. This deficiency in the PC-BOSS design used in Atlanta has been corrected in subsequent studies by addition of a flow equilibration chamber before removal of the side-stream.

Comparison of the PM_{2.5} FRM sulfate to the minor flow sulfate present on either the Teflon or Quartz filters (T_1 or Q_1 in Fig. 1), gave a particle concentrator efficiency (including absolute losses, Ding et al., 2001) of $50.0 \pm 4.0\%$ ($n = 20$) with a 95% confidence interval ($n = 20$). This value for the concentrator efficiency is at the lower end of values of 50–70% obtained in previous studies using the PC-BOSS (Ding et al., 2001; Eatough et al., 1999). Efficiencies for sulfate, soot and organic material have been similar in past PC-BOSS studies (Ding et al., 2001; Pang et al., 1999). An efficiency of 50% was used to correct for the concentration of species determined in the minor flow of the system.

4.2. Efficiency of the BOSS denuder

Previous studies (Cui and Eatough, 1998; Eatough, 1999; Ding et al., 2001) have indicated that the collection efficiency of the diffusion denuder for gas phase materials is not degraded over 2 months under continuous operation at 40 l/min. Denuder efficiency is determined by placing a quartz filter between the particle concentrator and the BOSS diffusion denuder. Thus, only gas phase compounds not removed by the denuder are collected by the Q_1 and C_1 filters. No carbonaceous material was found on the Q_1 filters during efficiency measurements. Therefore, the denuder removes all gas phase organic material which can be adsorbed by quartz, eliminating any positive quartz filter artifact.

The C_2 filter of the side-flow filter pack, Fig. 1, collects gas phase organic material. Therefore, in this study the efficiency was calculated as

$$\text{Efficiency} = 1 - C_1/C_2, \quad (1)$$

where, C_1 and C_2 are the carbonaceous material collected on filters C_1 and C_2 in Fig. 1. The obtained collection efficiency was $98.3 \pm 1.6\%$ for the period from 3 to 30 August 1999.

With this efficiency, the concentration of gas phase organic compounds after the denuder was calculated to vary from 0.3 to $1.4 \mu\text{g SVOC}/\text{m}^3$, and averaged $0.4 \mu\text{g SVOC}/\text{m}^3$. For concentrations of SVOC above $2 \mu\text{g}/\text{m}^3$ the breakthrough averaged 17% of the SVOC. For concentrations between 1 and $2 \mu\text{g}/\text{m}^3$ the breakthrough averaged 22% of the SVOC concentration. Below $1 \mu\text{g SVOC}/\text{m}^3$, the breakthrough averaged 80% of the measured SVOC concentration. The data have been corrected for the calculated breakthrough.

4.3. Inter- and intra-system sulfate comparisons

Table 1 lists the various intra- and inter-system sulfate concentration comparisons. To evaluate the precision of the PC-BOSS minor flow data, sulfate concentrations obtained on the two parallel channels were compared. The bias between the two data sets was $0.4 \mu\text{g}/\text{m}^3$, σ was $0.3 \mu\text{g}/\text{m}^3$, and r^2 was 0.96 ($n = 27$). No data pairs differed by more than 2σ . A two-tailed two-sample t -test on the data at the 5% rejection region was not statistically significant (a p -value of 0.58). When a statistical analysis report that results from a comparative experiment with two treatments is statistically significant, the difference between the two treatments is too large to claim that the difference is likely due to chance. The minor flow quartz and Teflon sulfate data were in agreement. Collocated PC-BOSS sulfate concentrations were also compared, and results shown in Table 1 indicate agreement in sulfate concentrations between the two similarly configured samplers. Comparison of weighed particulate mass on equilibrated Teflon filters from T_1 in Fig. 1, and constructed stable mass from the quartz and Teflon filters did not show a statistically significant difference (p -value of 0.91, Table 1). Fig. 2 shows a plot for this comparison. The PC-BOSS constructed stable mass was calculated as the sum of the average ammonium sulfate obtained from the Teflon, T_1 , and quartz, Q_1 , filters, Fig. 1; the average ammonium nitrate from the same Teflon and quartz filters; the soot collected on the quartz, Q_1 , filter; and the organic material retained on the same quartz filter, assuming a 61% carbon composition (Turpin and Lim, 2001). The PC-BOSS average T_1 and Q_1 concentrator efficiency adjusted sulfate concentrations and FRM sulfate concentrations for the 24h samples were comparable as shown in Table 1 and Fig. 3.

4.4. Non-volatile and semi-volatile particulate carbonaceous material

The concentration of organic material was estimated by multiplying the measured organic carbon content by 1.6. A factor of 1.4 was first derived by White and Roberts (White and Roberts, 1977) on the basis of measurements by Grosjean and Friedlander (Grosjean and Friedlander, 1975) from organic compounds sampled in an urban atmosphere. Some researchers (Saxena et al., 1995) however have questioned the validity of this ratio. A recent review of the literature (Turpin and Lim, 2001) suggests the factor of 1.6 (61% C) is a better value for urban environments.

The presence of significant fractions of carbonaceous material in urban aerosols resulting from direct emissions from stationary and automotive sources as well as from photo-oxidation of gaseous hydrocarbons has long been recognized (Grosjean, 1984), and results obtained from the Atlanta study was no exception. The average concentrations of particulate carbonaceous material in $\text{PM}_{2.5}$ were distributed as follows: non-volatile organic material averaged $11.4 \mu\text{g}/\text{m}^3$, SVOC lost from particles averaged $5.3 \mu\text{g}/\text{m}^3$, and soot averaged $1.5 \mu\text{g}/\text{m}^3$. Concentrations ranged from 1.3 – $12.6 \mu\text{g}/\text{m}^3$ for SVOC, from 3.7 – $21.0 \mu\text{g}/\text{m}^3$ for non-volatile organic material, and from 0.5 – $3.0 \mu\text{g}/\text{m}^3$ for soot, Fig. 4. Carbonaceous material (both elemental and organic) constituted an average of 51% of the total $\text{PM}_{2.5}$ composition determined with the PC-BOSS in this study. An average of 88% of the total carbon was organic. Of the total organic content, 32% was SVOC lost from particles during sampling and collected on the CIF adsorbent filter, C_1 in Fig. 1. This lost organic material, a negative artifact, would have resulted in an average 15% underestimation of total $\text{PM}_{2.5}$ mass if a single filter sampler were employed (Fig. 5).

The diurnal distribution pattern in the $\text{PM}_{2.5}$ composition from data obtained during the two 12 h sampling periods on even numbered days indicated that concentrations of non-volatile particulate organic material (those retained on the Quartz filter) and SVOC lost from particles were generally higher in the daytime than nighttime, Figs. 6 and 7. This trend could be due to photo-oxidation of gaseous hydrocarbons that is likely to occur in the daytime. Also, emissions from stationary and mobile sources, including material transported to the site, could be higher during daytime as compared to nighttime periods. However, if organic material originated only from local sources, mixing depths would tend to favor higher nighttime, as compared to daytime concentrations. Therefore, the higher daytime concentrations must reflect a combination of higher daytime emissions, daytime production of SVOC and possible transport of organic material from outside the urban area.

Table 1

Results of statistical analysis of PC-BOSS data. Both regression calculated (in parentheses) and zero intercept linear regression results are given

Comparison (<i>x</i> and <i>y</i>)	<i>n</i>	<i>r</i> ² Slope intercept	\bar{x}	Bias ($\mu\text{g}/\text{m}^3$)	σ ($\mu\text{g}/\text{m}^3$)	Probability (2-tailed 2-sample <i>t</i> -test at the 95% level)
Minor flow Teflon and quartz sulfate	27	0.96 (0.96) 1.07 ± 0.02 (1.04 ± 0.04) 0 ± 0.55 (0.21 ± 0.55)	5.2	0.4	0.25	0.58
PC-BOSS side-flow and FRM sulfate	7	0.95 (0.95) 0.083 ± 0.03 (0.83 ± 0.08) 0 ± 1.03 (0.01 ± 1.13)	12.0	2.0	4.1	
Adjusted PC-BOSS and FRM sulfate	12	0.88 (0.89) 1.03 ± 0.03 (0.91 ± 0.10) 0 ± 1.33 1.47 ± 1.30	11.2	0.5	0.8	0.75
Collocated PC-BOSS sulfate	4	0.85 (0.86) 1.02 ± 0.05 (1.53 ± 0.23) 0 ± 2.07 (−10.5 ± 0.33)	20.0	0.2	1.3	0.95
Collocated PC-BOSS non-volatile organic material	3	(0.31) 1.03 ± 0.14 (0.49 ± 0.74) 0 ± 2.92 (6.83 ± 3.31)	12.0	0.8	1.5	0.77
Collocated PC-BOSS SVOC	3	(0.75) 0.70 ± 0.29 (−0.15 ± 0.08) 0 ± 2.23 (4.19 ± 0.28)	4.0	0.4	1.5	0.77
Weighed Teflon filter mass vs. constructed PM _{2.5} non-volatile mass	20	0.66 (0.94) 1.03 ± 0.03 (1.12 ± 0.08) 0 ± 3.14 (−2.92 ± 0.5)	27.7	0.4	3.2	0.91

4.5. Fine particulate ammonium sulfate

The average concentration of fine particulate PM_{2.5} sulfate was about 50% higher than the non-volatile organic material, but about equal to the sum of nonvolatile and SVOC organic material, Figs. 4 and 5. The average sulfate concentration for the August 1999 sampling program was 12.2 μg sulfate/ m^3 , or 17.0 $\mu\text{g}/\text{m}^3$ as ammonium sulfate, and varied from 2.8–28.5 $\mu\text{g}/\text{m}^3$ ammonium sulfate. Ammonium sulfate averaged 47%

of the total PM_{2.5} fine particulate composition from the PC-BOSS data. The diurnal trends for ammonium sulfate concentrations were similar to that discussed above for organic material, Figs. 6 and 7, in that daytime concentrations were generally higher than the nighttime concentrations. This is also consistent with the increased importance of photochemistry leading to the formation of sulfate during the day. The higher daytime sulfate concentrations could also be due to greater daytime mixing of regionally transported pollutants.

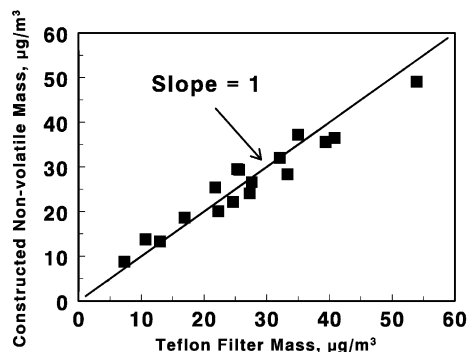


Fig. 2. Comparison of T_1 (see Fig. 1) measured mass and PC-BOSS constructed non-volatile $PM_{2.5}$.

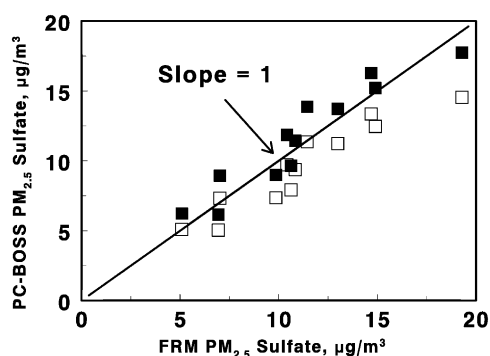


Fig. 3. Comparison of $PM_{2.5}$ FRM and PC-BOSS calculated sulfate (closed squares). The PC-BOSS efficiency is based on the FRM data. The PC-BOSS sulfate concentrations calculated using the side flow PC-BOSS data are also given as the open squares for comparison, see text.

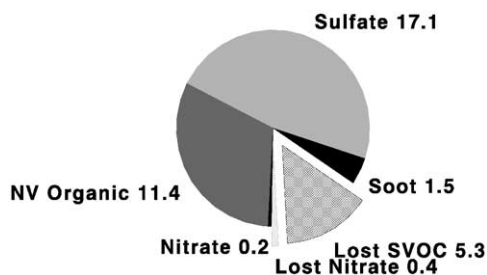


Fig. 5. Average $PM_{2.5}$ composition obtained from PC-BOSS data during the Atlanta EPA Supersite study. Sulfate and nitrate are calculated as their ammonium salts. Organic material is assumed to be 61% C.

4.6. Fine particulate ammonium nitrate

Several studies have shown that aerosols in most parts of the eastern United States contain insignificant fractions of nitrate (Andrews et al., 2000). Results from the Southeastern Aerosol and Visibility Study (SEAVS) compiled by Andrews et al. indicated that nitrate concentrations in most parts of the Southeastern United States ranged from 0.1 to 0.3 $\mu\text{g}/\text{m}^3$ ammonium nitrate. Results obtained with the PC-BOSS indicated that the average concentration of nitrate (expressed as ammonium nitrate) retained on both the quartz and Teflon filters for the Atlanta study was 0.2 $\mu\text{g}/\text{m}^3$. However, ammonium nitrate lost from the quartz and Teflon filters and trapped by the Nylasorb and CIF filters (C_1 and N_1 in Fig. 1) averaged 0.4 $\mu\text{g}/\text{m}^3$. The nitrate content of the particles sampled in Atlanta was low compared to particulate sulfate concentrations, and the filter retained nitrate concentration is in agreement with

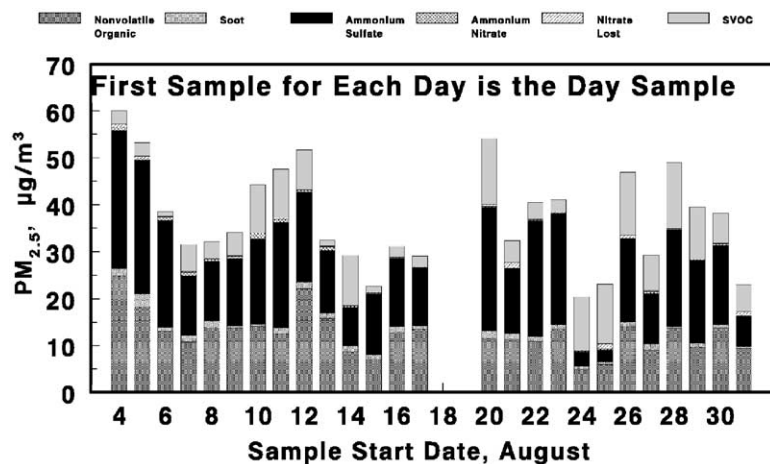


Fig. 4. Daily composition of $PM_{2.5}$ obtained from PC-BOSS data during the Atlanta EPA Supersite study. Sulfate and nitrate are calculated as their ammonium salts. Organic material is assumed to be 61% C.

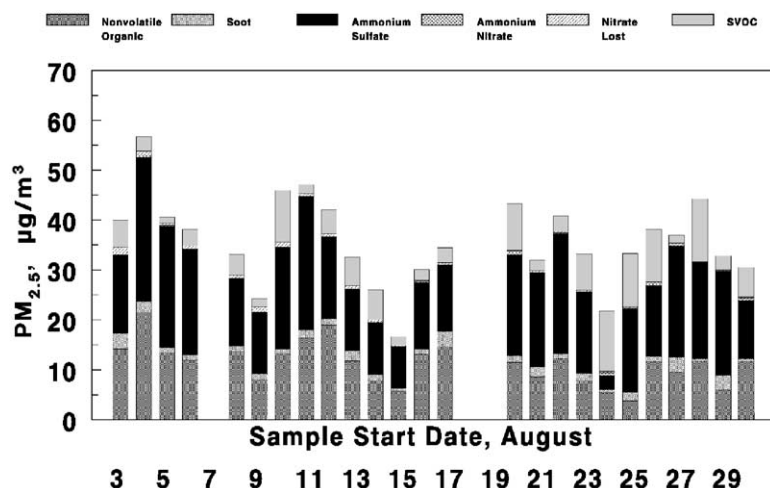


Fig. 6. Even-day and -night composition of $PM_{2.5}$ obtained from PC-BOSS data during the Atlanta EPA Supersite study. The first set of data for each date are the daytime concentrations. Sulfate and nitrate are calculated as their ammonium salts. Organic material is assumed to be 61% C.

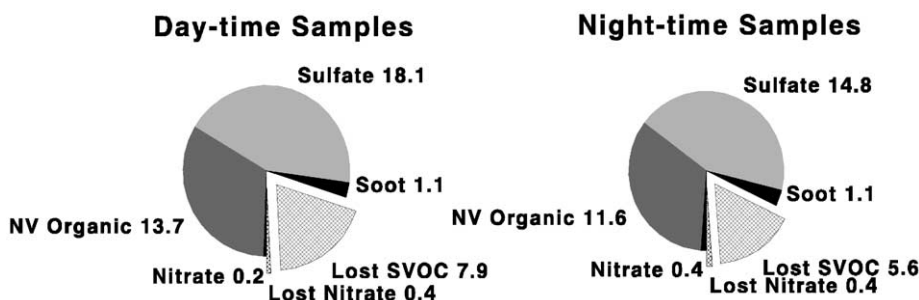


Fig. 7. Average day-time and night-time $PM_{2.5}$ composition obtained from PC-BOSS data during the Atlanta EPA Supersite study. Sulfate and nitrate are estimated as their ammonium salts. Organic material is assumed to be 61% C.

results reported by Andrews et al. for the SEAVS study of 1995 as well as with the historical evidence for the inverse relationship between sulfate and nitrate concentrations in the east (Hidy, 1974). The low nitrate content of the particles could be attributed to the predominantly acidic environment with most of the nitrate being present as nitric acid as described earlier in the introductory section of this article (Harker et al., 1977; Appel et al., 1980a). The PC-BOSS data does indicate that the nitrate content would be underestimated by an average of 67% as a result of the loss of ammonium nitrate from collected particles for single filter data.

5. Conclusions

The PC-BOSS was effective in eliminating positive quartz filter artifacts and also accounting for negative

artifacts for the determination of nitrate and organic material in fine particulate matter in Atlanta. The side-flow diversion prior to the particle concentrator was intended to determine the particle concentrator efficiency. However, the short distance before removal of the side flow proved to be insufficient for particle equilibrium across the sample tube. Therefore, sulfate data from the PC-BOSS major flow after the denuder and sulfate obtained from the $PM_{2.5}$ FRM sample were used for the calculation of particle concentrator efficiency. A mixing chamber prior to the side-flow diversion will be used in future uses of the sampler. The results obtained with the PC-BOSS indicated significant semi-volatile fine particulate organic material was present in the aerosols sampled during the Atlanta Supersite Study, averaging 32% of the fine particulate organic material and 15% of the fine particulate mass.

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